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Effect of group composition of the vacuum distillate from heavy Kazakhstan and West Siberian oil on the yield of light fractions during the catalytic cracking

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Abstract

This paper presents the research results aimed at the assessment of the impact of the group composition of Kazakhstan and West Siberian heavy vacuum distillate on the yield and composition of the catalytic cracking products. The laboratory research was performed to determine the physical and chemical characteristics and group composition of two samples of the heavy vacuum distillate of Kazakhstan and West Siberian oil. The patterns of changing yield of wet gas, light and heavy gas oil, coke, and gasoline depending on the composition of the feedstock were established using mathematical model of catalytic cracking.

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Keywords: deep processing, vacuum distillate, physico-chemical characteristics, group composition, mathematical model, wet gas, gasoline

1. Introduction

The worldwide trend to increasing the depth of petroleum feedstock processing and to improving the environmental specifications of motor fuels is directing the refinery industry on the construction of new and reconstruction of existing oil processing units that allows to produce valuable light fractions from heavy oil residue [1-3].

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Thus, oil and oil feedstock, extracted from them for refining processes, are significantly different in physical and chemical characteristics, depending on the geographical location of oil fields, the depth and geological age [4,5]. The difference in the physical and chemical indicators of oil is directly related to the methods of transportation and refining of crude oil and the quality of oil products obtained from them.

Products yield from catalytic cracking unit may significantly vary depending on the feed composition, hydrodynamic regimes, process conditions, catalysts type and etc. [6-9]. Application of the mathematical models allows adjusting the process conditions of industrial refining unit, taking into account the composition of the feedstock to provide the desired ratio of petroleum product and quality in accordance with international environmental requirements [10-20].

Laboratory researches to determine the group composition of two samples of vacuum distillate from Kazakhstan and West Siberian oil obtained by vacuum distillation of fuel oil and directed as a raw material in the catalytic cracking work were conducted in this research.

The aim of research is to evaluate the effect of group composition of a vacuum distillate from Kazakhstan and West Siberian oil on the yield and composition of catalytic cracking products using a mathematical model.

2. Study subject

The study subject is a catalytic cracking unit, part of a combined installation of fuel oil CT-1/1 deep processing.

Vacuum distillate after vacuum distillation (C-001) is directed to the hydrotreatment unit (C-100), after that is used as feedstock for catalytic cracking unit (P-200). Wet gas, unstable gasoline (end boiling point of 195 or 205°C), light (195 - 310°C) and heavy gas oil (310 - 420°C) and slop containing catalytic dust (fr.> 420 C) are products of C-200 section. Wet gas and unstable gasoline from section C-200 is directed to the C-300 section, where gasoline stabilization, gas cleaning and gas separation to formation a propane-propylene and butane-butylene fraction and stable gasoline occur.

The cracking of vacuum distillate hydrocarbons occurs on the surface of the zeolite powdered catalyst in a riser reactor with continuous regeneration of the coked catalyst [21, 22].

The process conditions of the reactor-regenerator block of C-200 section KT-1/1 unit are shown in Table 1.

Table 1. Process conditions of the reactor-regenerator block of catalytic cracking unit.

Parameter of process conditions	Value
Consumption of feedstock, m3/h	160-420
Temperature of feedstock, °C	240-350
Steam consumption in the reaction zone, kg/h	2000-14000
Steam consumption in the desorber top, kg/h	No less than 1400
Steam consumption in the middle part of desorber, kg/h	No less than 360
Steam consumption in the desorber bottom, kg/h	No less than 360
Process temperature, °C	495-535
Pressure, Pa	78453,2-156906
Temperature of the regenerated catalyst, °C	630-700
Catalyst/feedstock ratio, tonnecat/tonnefeed	5-9

Process conditions of riser reactor can vary significantly depending on the required yield of wet gas, gasoline and diesel fractions, types of catalysts and characteristics of the feedstock.

3. Approaches and methods

Group composition of two samples of vacuum distillate from Kazakhstan and West Siberian was determined by gas-adsorption chromatography as described in VNII NP [23].

The sulfur content of catalytic cracking feedstock was determined by X-ray fluorescence analysis using "SPECTROSCAN SL» sulfur analyzer (operating range of sulfur concentrations of 0.0007 - 5.0%, the lower limit of sulfur detection 0.0005%).

To measure the density of the raw materials samples was used viscometer Stabinger "Stabinger ViscometerTM SVMTM 3000" measuring range of density from 0.65 to 3.0 g/cm3.

Impact assessment of group composition of vacuum distillate from Kazakhstan and West Siberian oil was made using the mathematical modeling method.

The calculations were performed using catalytic cracking mathematical model of riser reactor developed at the department of Fuel Engineering and Chemical Cybernetics of Tomsk Polytechnic University.

The catalytic cracking mathematical model is based on the formalized scheme of hydrocarbons conversions [24] according the results of liquid-chromatographic adsorption separation of feedstock and cracking products, gas chromatography-mass spectrometry, gas chromatography and structural-group composition methods of petroleum products.

Thermodynamic analysis of the reactions was performed according to the results of laboratory research using quantum chemical methods of calculation [25], the formalized scheme of hydrocarbons conversion and the mathematical model of catalytic cracking was composed. The differential equations system is solved by the 4th order Runge-Kutta method with initial conditions τ = 0, Ci = Ci0, T0 = Tkat, l=0.

$$
\begin{cases}
\frac{dC_{paraffinsHMW}}{d\tau} = -k_1 C_{paraffinsHMW} - k_2 C_{paraffinsHMW}; \\
\frac{dC_{paraffinsMMW}}{d\tau} = k_1 C_{paraffinsHMW} - k_3 C_{paraffinsMMW} - k_4 C_{paraffinsMMW} + k_{-4} C_{isoparaffins}; \\
\frac{dC_{isoparaffins}}{d\tau} = k_2 C_{paraffinsHMW} + k_4 C_{paraffinsMMW} - k_{-4} C_{isoparaffins} - k_5 C_{isoparaffins} + k_7 C_{olefins} C_{naphthenes}; \\
\frac{dC_{olefins}}{d\tau} = k_1 C_{paraffinsHMW} + k_2 C_{paraffinsHMW} - k_6 C_{olefins} + k_{-6} C^2_{gas} - k_7 C_{naphthenes} C_{olefins} + k_8 C_{naphthenesHMW} \\
+ k_9 C_{aromatics} - k_{13} C_{olefins} - \\
- k_{-9} C_{monoaromatics} C_{olefins} + k_{-13} C_{naphthenes} + k_{14} C_{monoaromatics} - k_{-14} C_{olefins} C_{monoaromatics}; \\
\frac{dC_{gas}}{d\tau} = 2k_3 C_{paraffinsMMW} + 2k_5 C_{isoparaffins} + 2k_6 C_{olifins} - 2k_{-6} C^2_{gas}; \\
\frac{dC_{naphthenes}}{d\tau} = k_8 C_{naphthenesHMW} - k_7 C_{naphthenes} C_{olefins} + k_{13} \mathrm{C_{olefins}} - k_{-13} \mathrm{C_{naphthenes}}; \\
\frac{dC_{monoaromatics}}{d\tau} = k_7 C_{naphthenes} C_{olefins} + k_9 C_{aromatics} - k_{14} \mathrm{C_{monoaromatics}} - k_{-9} C_{monoaromatics} C_{olefins} + \mathrm{k_{-14}} C_{olefins} \mathrm{C_{monoaromatics}}; \\
\frac{dC_{naphthenesHMW}}{d\tau} = -k_8 C_{naphthenesHMW} - k_{10} C_{naphthenesHMW}; \\
\frac{dC_{aromatics}}{d\tau} = -k_9 C_{aromatics} + k_{-9} C_{monoaromatics} C_{olefins} + k_{10} C_{naphthenesHMW} - 2k_{11} C^2_{aromatics}; \\
\frac{dC_{resins}}{d\tau} = k_{11} C^2_{aromatics} - k_{12} C_{resins}; \\
\frac{dC_{coke}}{d\tau} = k_{12} C_{resins} \\
\frac{dC_{H_2}}{d\tau} = 3k_{10} C_{naphthenesHMW} + k_{11} C^2_{aromatics} + 2k_7 \mathrm{C_{olefins}} \mathrm{C_{naphthenes}}; \\
\frac{dT_c}{dl} = (\alpha a_v (T - T_c) - \sum_{i=1}^{n} (\Delta H_i W_i)) / (\omega \rho c)
\end{cases}
\qquad (1)
$$

where dCi is change in concentration of the corresponding i-th hydrocarbon group; τ is contact time; k is rate constant; ω, ρ, c are velocity, density and specific heat flow, m/sec, kg/m3, kcal/kg·K; Tc is temperature of the feedstock, K; T is flow temperature, K; Tkat is catalyst temperature after regeneration, K; α is heat transfer coefficient kcal/m2·s·K; αv is catalyst specific surface area, m2/m3; ΔHi is enthalpy of i-th component formation,

kcal/mol; Wi is rate of chemical reaction, mol/m3·s; HMW paraffins and MMW are high molecular weight (C13-C40) and medium weight (C5-C11+) paraffins, HMW naphthenes (mono and bi-cycloalkane with long alkyl substituents).

The mathematical model of catalytic cracking allows calculating the composition of stream after the reactor, the yield of gasoline fraction, wet gas, coke, light and heavy gas oil, group composition of gasoline fraction and the octane number of gasoline. Thus, the model predicts the yield and composition of the cracking products, also important environmental performance of catalytic cracking gasoline – the content of aromatic hydrocarbons, benzene and olefins.

To the impact assessment of feedstock composition on the catalytic cracking product, calculations on the model for vacuum distillate from Kazakhstan and West Siberian oil at fixed parameters of technological modes were performed: consumption of feedstock 380.5 m3/h, inlet reactor temperature for feedstock 317.4 ° C, the total consumption of steam in the reaction zone of 8105.8 kg/h, total steam to the desorption zone 6966.9 kg/h, the temperature at the exit of the ballistic separator 520. 0 °C, the pressure in the settling zone 14219.642 Pa, regenerated catalyst temperature 692.0 °C, catalyst/feedstock ratio 4.99 tonnecat/tonnefeed.

4. Results and discussion

Table 2 presents the results of laboratory tests to determine the physical and chemical characteristics of the two samples of a vacuum distillate from Kazakhstan (VD-1) and West Siberian oil (VD-2).

Table 2. Physical and chemical characteristics of the catalytic cracking vacuum distillate.

Hydrocarbon group	Vacuum distillate content, % wt.	
	VD-1	VD-2
Paraffins + naphthenes	73.13	58. 85
Aromatic hydrocarbons	23.31	38.00
Alcohol benzene resin	3.56	3.15
Density at 15, °C	0.887	0.9052
Fractional composition, °C	296.0-530.0	294.0-569.0
Sulfur content, % wt.	0.1175	0.051

According to Table 2, a vacuum distillate obtained at the vacuum distillation of Kazakhstan oil (VD-1), is characterized by a high content of saturated hydrocarbons in comparison with vacuum distillate from the West Siberian oil (VD-2). The ratio of saturated hydrocarbons to aromatics (VD-1) is 3.14, for VD is 2 1.55. VD-1 is characterized by more light fractional composition: 50% boils at the temperature of 410 ° C, while the VD-2 - 441 ° C, the sulfur content in the feedstock from Kazakhstan oil above 0.1175 % wt. regarding VD-2 – 0.051 % wt.

Calculations on catalytic cracking model (Fig.1) showed that the yield of wet gas (16.7 wt%) and a gasoline fraction (60.08 % wt.) is higher during the catalytic cracking of vacuum distillate obtained from Kazakhstan oil (with high content of saturated hydrocarbons – 73.13 % wt.) relative to the vacuum distillate obtained from West Siberian oil (with high content of aromatic hydrocarbons – 58.85 % wt.) - (15.3 and 56.2 % wt.).

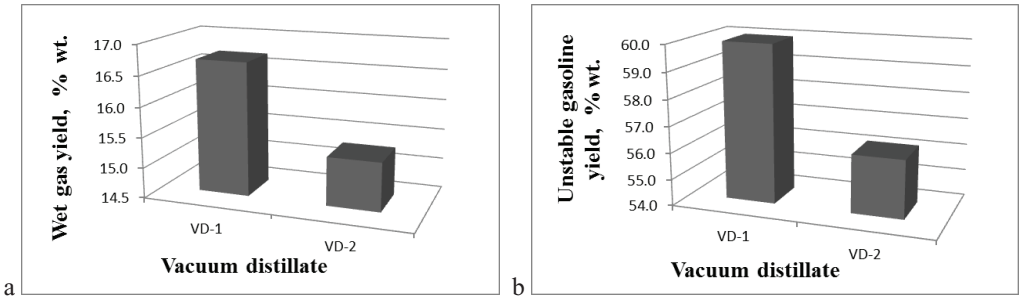


Fig. 1. Yield of wet gas (a) and unstable gasoline (b) depending on the composition of feedstock.

Calculations on the models show the yield of the gasoline fraction with same octane characteristic varies during a catalytic cracking of vacuum distillate with various group compositions at the same process conditions.

Table 3. Group composition of gasoline from catalytic cracking

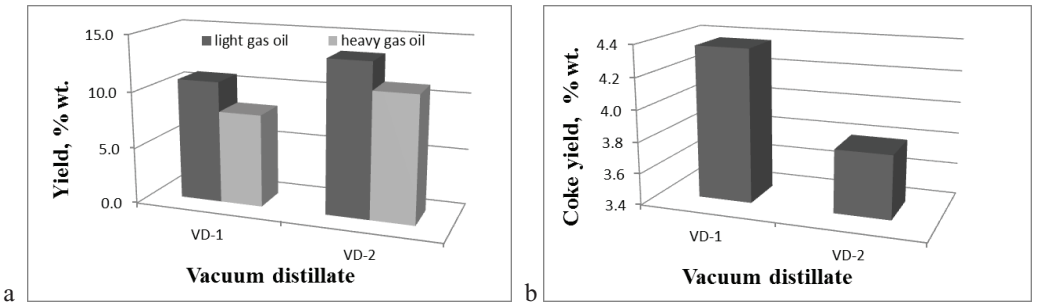
Hydrocarbon group	VD-1	VD-2
Paraffins	5.06	3.87
Isoparaffins	35.52	27.44
Naphthenes	18.73	19.55
Olefins	11.49	9.86
Aromatic hydrocarbons	30.82	36.71
Research octane number	91.30	91.70
Motor octane number	82.60	82.90

Thus, gasoline fraction from catalytic cracking unit obtained during the processing of vacuum distillate from Kazakhstan oil is characterized by a high content of isoparaffinic hydrocarbons (35.52 % wt.) and olefins (11.49 % wt.) and a lower content of aromatic hydrocarbons (30.82 % wt.). Such a composition of the gasoline fraction is directly related to group composition of the feedstock (VD-1), which is characterized by a high content of paraffinic and naphthenic hydrocarbons (73.13 % wt.) due to the paraffinic hydrocarbons cracking reactions followed isomerization and hydrogen transfer with formation of isoparaffins and aromatic hydrocarbons.

At the same time gasoline fraction obtained during the processing of vacuum distillate from the West Siberian oil, contains a higher content of aromatic hydrocarbons (36.71 wt.%) and naphthenes (19.55 wt.%) due to the intensive reactions involving aromatic hydrocarbons (aromatics dealkylation, cracking naphthenes, hydrogen transfer).

The yield of olefin hydrocarbons in gasoline is above during processing of vacuum distillate from the Kazakhstan oil (VD-1 – 11.49 % wt., VD-2 – 9.86 % wt.). The benzene content is higher during processing of vacuum distillate from the West - Siberian oil (VD-1 – 0.64 % wt., and VD-2 – 0.76 % wt.), which imposes restrictions on using the catalytic gasoline cracking in gasoline blending process.

The yield of light and heavy gas oil is above during processing of vacuum distillate obtained from the West Siberian oil (VD-2) (Fig. 3) and containing a large concentration of aromatic hydrocarbons in composition (VD-2 – 38.00% by weight, the VD-1. – 23.31% by weight).



a b

Fig. 2. Yield of light, heavy gas oil (a) and coke (b) depending on the composition of feedstock.

The coke yield is higher during processing of vacuum distillate from the Kazakhstan oil (4.4 % wt. – VD-1, 3.80 wt.% – VD-2) due to a high content of resins (3.56% by weight.) in comparison with vacuum distillate from the West Siberian oil (3.15 % wt.), and reactions of aromatic and resinous substances condensation with coke formation carry out more intensive (Fig.2).

5. Conclusion

It is determined, based on the results of laboratory research to determine the group composition of the catalytic cracking feedstock from Kazakhstan and West Siberian oil, the vacuum distillate from the Kazakhstan oil is beneficial in catalytic cracking technology from the standpoint of obtaining a high yield of gasoline fraction and wet gas rich in propane-propylene fraction of and butane-butylene fraction, as the vacuum distillate composed of more than 70% of saturated hydrocarbons. The yield of wet gas and the gasoline fraction is higher due to the reactions of cracking and isomerization of paraffins, dealkylation of naphthenes and hydrogen transfer with formation isoparaffins and aromatic hydrocarbons.

Thus coke yield during the catalytic cracking of Kazakhstan vacuum distillate is higher (4.4% wt.), which is associated with a higher content of resins in the catalytic cracking feedstock relative to the vacuum distillate from the West Siberian oil (3.80 % wt.). Therefore, it is important to predict the coke yield, depending on the composition of the feedstock and process conditions with using system of strategy analysis. For example, in the case of a "hard" temperature mode in a riser reactor, a high yield of coke on the catalyst may promote the reducing the catalyst activity and lead to unbalanced temperature mode of "riser regenerator" conjugated system.

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